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Acid Deposition and Watershed Characteristics in Relation to Lake Chemistry in Northeastern Minnesota

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16. ABSTRACT

The relationship between lake sensitivity to atmospheric acidic inputs and the neutralization capacity of watersheds is examined for 267 lakes in northeastern Minnesota. Three water chemistry/sensitivity measures (color, sulfate, and alkalinity) are correlated with variables representative of precipitation and sulfate inputs, hydrology, and the acid neutralization capacity of various watershed components. An ordinal scale for ranking bedrock and surficial deposit neutralization capacity is presented. The watershed variables found to account for the largest percentages of the variability in measured color, sulfate, and alkalinity levels are determined. Color is strongly related to the presence of peat or marsh and hydrologic renewal time, whereas sulfate is primarily related to atmospheric deposition, evaporative concentration, bedrock type, and the presence of coniferous forest. Variation in alkalinity is the most difficult of the water chemistry measures to explain; for headwater lakes, atmospheric sulfate input, water renewal time, the presence of deciduous forest, and the weatherability of underlying bedrock determine much of its variability. The results illustrate important averaging properties of watersheds from small headwater systems to large drainages and the difficulty in obtaining correlations for some water quality measures (e.g., alkalinity) when some variables, such as soils and land cover, are available only as large-area averages.

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ACID DEPOSITION AND WATERSHED CHARACTERISTICS IN RELATION TO LAKE CHEMISTRY IN NORTHEASTERN MINNESOTA

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The relationship between lake sensitivity to atmospheric acidic inputs and the neutralization capacity of watersheds is examined for 267 lakes in northeastern Minnesota. Three water chemistry/sensitivity measures (color, sulfate, and alkalinity) are correlated with variables representative of precipitation and sulfate inputs, hydrology, and the acid neutralization capacity of various watershed components. An ordinal scale for ranking bedrock and surficial deposit neutralization capacity is presented. The watershed variables found to account for the largest percentages of the variability in measured color, sulfate, and alkalinity levels are determined. Color is strongly related to the presence of peat or marsh and hydrologic renewal time, whereas sulfate is primarily related to atmospheric deposition, evaporative concentration, bedrock type, and the presence of coniferous forest. Variation in alkalinity is the most difficult of the water chemistry measures to explain; for headwater lakes, atmospheric sulfate input, water renewal time, the presence of deciduous forest, and the weatherability of underlying bedrock determine much of its variability. The results illustrate important averaging properties of watersheds from small headwater systems to large drainages and the difficulty in obtaining correlations for some water quality measures (e.g., alkalinity) when some variables, such as soils and land cover, are available only as large-area averages.

Introduction

The geochemistry of the substrate underlying watersheds in the Canadian Shield region of Minnesota has been viewed as the dominant factor controlling the generally low buffering capacity of these surface waters (Galloway and Cowling, 1978; Schindler, 1980; Glass and Loucks, 1980). However, surface water chemistry varies widely from lake to lake within the region, a response pattern believed to be attributable to the diverse ways in which watershed components (for example, geology, topography, hydrology, vegetation, land use) interact through weathering, detention, dilution, concentration, biotic/microbial activity, and the closely coupled oxidation/reduction-acid/base reactions to alter the chemistry of precipitation inputs (Schnoor and Stumm, 1985). Quantitative measurement of these watershed components is difficult, and information on how they alter atmospheric inputs to control the chemistry of lakes generally has been inadequate for predictive modeling of recent lake response to changes in precipitation chemistry (Glass and Brydges, 1982; Chen *et al.*, 1983).

To improve understanding of how watersheds control lake chemistry, a 5-year program to investigate chemical inputs, watershed characteristics, and lake responses was begun in 1979 by the University of Minnesota–Duluth (UMD) and the U.S. Environmental Protection

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Agency Environmental Research Lab—Duluth (ERL-D). Data on lake and watershed properties were collected for 267 watersheds in northeastern Minnesota with the goal of testing the relationships between watershed characteristics and the resultant lake water quality.

Many northeastern Minnesota lakes are characterized by colored water due to high concentrations of dissolved organic matter, often bonded with Fe, Al, and other metals (Shapiro, 1966; Reuter and Perdue, 1977). The importance of these humic substances as a factor contributing to acidity and pH, and in controlling the speciation and bioavailability/toxicity of metals is well established (Stumm and Morgan, 1981; Brosset, 1978; Oliver *et al.*, 1983; Glass, 1977; Perrin and Dempsey, 1974); therefore they need to be considered in addition to the total alkalinity and pH buffering capacity of the receiving system in evaluating the overall response of watersheds to atmospheric inputs.

Sulfate, a strong-acid anion, may constitute a substantial part of the ionic balance of acidity observed in precipitation and often remains as a major constituent in surface water systems sensitive to acidification (Overrein *et al.*, 1980; Thompson and Hutton, 1985). All precipitation contains substances from atmospheric washout, with dissolved CO_2 and, usually, small quantities of SO_4^{2-} and NO_3^-, contributing to the normally slightly acid state of precipitation in some remote regions of North America (Glass and Loucks, 1980; Harvey *et al.*, 1981; National Research Council, 1981). In addition to the input of sulfate from precipitation, watershed factors that contribute sulfur need to be considered. In this region, bedrock weathering is the primary potential source of nonatmospheric sulfur in the watershed.

The principal means of neutralizing strong acid inputs to surface waters can be defined and measured as the total acid neutralizing capacity or alkalinity (Stumm and Morgan, 1981). However, a watershed also has a neutralizing capacity that depends in part on the mineralogy of the surficial materials (Shilts, 1981), on the bedrock geology (Kramer, 1978), and on biological interactions with constituent minerals and humic materials (Schnoor and Stumm, 1985). The goal of this paper is to evaluate the influence of these watershed components/processes on atmospheric deposition as it reaches the subtending lake basin.

Research Framework and Hypotheses

The primary unit of analysis used in this study for examining relationships between atmospheric inputs, watershed factors, and lake response is the lake/watershed system. Various studies (Chen *et al.*, 1983; Schnoor *et al.*, 1984) have incorporated a limited set of the factors and processes considered important in watershed studies: atmospheric inputs of water and chemicals, evaporation, canopy alteration of chemical concentrations in rainfall, watershed relief and runoff processes, surface water detention, terrestrial neutralization processes, and various permeability and below-ground hydrologic flow parameters. In addition to these important properties of biological processing and decomposition, chemical adsorption and acid formation or neutralization in watersheds are associated with vegetation and litter, soil biochemistry, bedrock and surficial mineralogy, and flow among various hydrologic compartments. In a mathematical model for predicting resultant aqueous alkalinity and pH in the receiving systems (lakes) of the study region, Schnoor *et al.* (1984) have proposed using water volume and alkalinity in each compartment, flowrates, cumulative base cation export, and a rate constant for acid neutralization by soil and minerals.

When all of the above are considered from the viewpoint of processes within a watershed, nine major classes of measurable watershed properties can be recognized as having the potential to influence the water chemistry of the responding system (Table 1). Each class of properties in the table has associated with it certain processes that have the potential for concentrating or consuming atmospheric inputs. The reaction rates for the processes listed in Table 1 all may be influenced by watershed size, the ratio of water surface area to terrestrial area, and the residence time of water within any component of the watershed. While in-lake processes

Table 1. Measurable properties and processes in watersheds.

Class of Property	Associated Watershed Processes
1. Atmospheric inputs	Precipitation and atmospheric deposition of water and chemicals.
2. Area	Interception of atmospheric inputs; evaporation and volatilization.
3. Relief	Surface and subsurface flow rates, transport of materials, and interception of atmospheric inputs.
4. Hydrology	Hydrologic exchange including lake water renewal rates and process reaction rates.
5. Lake morphometry	Lake volume and depth, water and energy transport, chemical/biological internal conversion, circulation, and material resuspension.
6. Bedrock geology	Weathering rates, geochemical reactions and surface and groundwater flows and quality.
7. Surficial deposits	Infiltration, ion exchange, neutralization, and weathering reactions.
8. Land cover type	Atmospheric deposition processes, evapotranspiration, element storage, decomposition, and ion exchange.
9. Land use	Hydrologic transport of materials, alteration of water quality, and subsurface flows.
10. Lake water chemistry	Net result of above processes

such as sediment interactions or groundwater inputs can be important, they are difficult to measure and were therefore not directly part of this study.

The classes of measurable properties constitute a conceptual model of how water and chemical inputs ("dose") and the resultant responses in the lake system are linked in a biogeochemical relationship:

$$\text{inputs} \times \text{watershed mediation (biogeochemical processes)} = \text{lake concentrations.}$$

The goal of this study was to examine the relationships intrinsic to this complex biogeochemical equation. While the inputs are relatively difficult to quantify, they are definable within a range of uncertainty; the watershed mediation term, however, is conceptually complex and involves all of the physical, chemical, and biological aspects of the watershed. The primary hypothesis is that the chemistry of water in the receiving system (lake) of a watershed will be a composite function of all antecedent water and chemical inputs and losses, and the processes affecting the reactive components in the water as it passes through the watershed.

This general hypothesis can be broken down into more testable subhypotheses for each chemical parameter of interest in the receiving system. The sensitivity of lake waters to acidic atmospheric inputs may be examined by looking at three water chemistry measures: color (a measure of organic acid buffering components and metal complexation capacity), sulfate (a measure of response from atmospheric inputs), and alkalinity (a measure of acid neutralizing capacity and watershed/in-lake processes). For these measures a series of testable subhypotheses is developed in the following sections to evaluate the influence of watershed factors on the concentration of chemical parameters in the lake.

Study Area

The study area stretches 130 km from north to south and 260 km east to west across Cook, Lake, and St. Louis counties in northeastern Minnesota (Fig. 1) and encompasses over 2,500 lakes, of which 267 have been sampled for the current study. Almost all (95%) of the lakes in this study are located within the Superior National Forest, Boundary Waters Canoe Area Wilderness (BWCAW), and Voyageurs National Park (VNP); as a result, direct anthropogenic influences are minimal. Most (80%) of the lakes drain through the Rainy Lake system into Hudson Bay, and the remainder, on the east side of the Laurentian Divide, drain into Lake Superior.

The region generally experiences continental climate. Annual precipitation ranges from 66 cm in the western portion of the study area to 76 cm near Lake Superior; two-thirds of the annual precipitation falls during the growing season. The area includes both the highest and lowest points in Minnesota: Eagle Mountain at 690 m and Lake Superior at 180.6 m. Away from Lake Superior

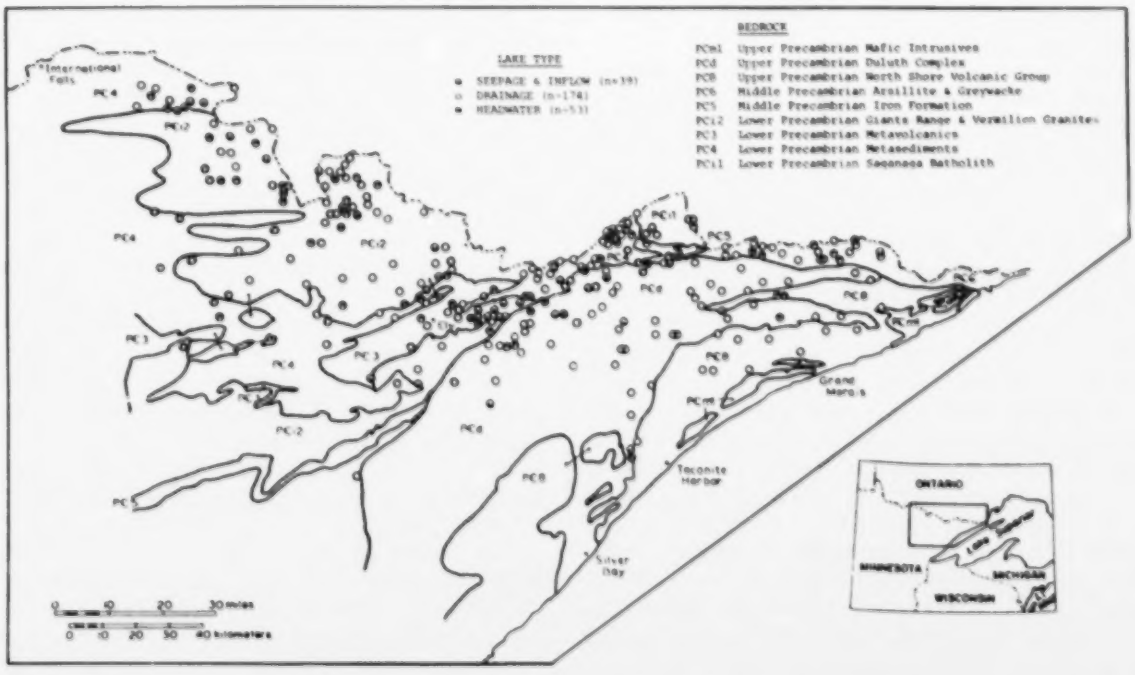

Fig. 1. Location of Minnesota Study Lakes by Hydrologic Type and Bedrock Geology (Bedrock geology from: Sims, P. K. 1970, Geologic Map of Minnesota Bedrock Geology. Minnesota Geological Survey, plate 1).

the topography is moderate, with the elevation of the study lakes ranging from 338 to 592 m.

Lake sensitivity criteria developed by Glass and Loucks (1980) were used in the selection of study watersheds in 1979 and 1981. An approximately equal number of sensitive and nonsensitive lakes with a balanced geographic distribution throughout the BWCAW-VNP region of northeastern Minnesota were chosen. These include many small headwater lakes as well as larger lakes that are a part of complex river drainage systems. The surface area of the lakes range from 1.2 ha to 89 $\times 10^3$ ha, with total watershed areas ranging from 8.8 ha to 3.8 $\times$ 10^6 ha. The hydrology of the lakes can be classified in a manner similar to that used by Eilers *et al.* (1983) as predominantly drainage systems (n = 176) with some headwater (n = 52), seepage (n = 30), and inflow (n = 9) lakes present. Morphometrically, the lakes vary in depth from 1 m to over 79 m, in volume from 6 $\times$ 10^3 to 5.5 $\times$ 10^9 m^3, with estimated water renewal times of 0.01 to 25.4 yr.

Bedrock underlying the region is predominantly Precambrian igneous and metamorphic rock. The surficial deposits are shallow, rocky tills from the recent Wisconsin glaciation with localized, poorly drained marshy areas and peat deposits. On the extreme western edge of the study area, Lake Agassiz clays and St. Louis Lobe calcareous tills are present. The central and eastern portions of the study area have noncalcareous Superior Lobe tills and outwash deposits, interfingered locally in the western region with calcareous material (Wright, 1972). Soils throughout the area are thin and poorly developed. Ground water storage and flows are generally not large due to the impermeable bedrock and shallow surficial deposits.

Sulfur occurs as a minor constituent in mafic intrusive rocks in northeastern Minnesota principally in the form of pyrite, FeS_2, but locally as other iron, copper, nickel, and arsenic sulfides. Estimates of the sulfur content of rock units are difficult because of the few available analyses and because of the extreme heterogeneity in its distribution within the rock bodies. Where sulfur was detected in 57 rock analyses, the content ranged from 0.01% to 1.6% and averaged 0.27% (Sims and Morey, 1972). In our own analysis of three rocks characteristic of the study region, we found a sulfur content of only 0.02%–0.04%. In a calibrated watershed study at Filson Creek and Omaday Lake, MN, which has disseminated sulfide deposits, groundwater concentrations were measured from 7 shallow wells in 1979 for sulfate and alkalinity; they were found to average 40.5 mg/L (range 4.7 to 215 mg/L) and 1720 μeq/L (range (122–4130 μeq/L), respectively (Siegal, 1981). However, the surface water concentrations were less than 5 mg/LSO_4^{2-} and alkalinity averaged 240 μeq/L, leading Siegal to conclude that, on average, the amount of sulfur entering the surface water from groundwater contacting these sulfide deposits was small compared to atmospheric loading.

Watershed Variables and Measurement Methods

Limnologists have long recognized the large number of watershed and lake-morphometric properties that influence lake water chemistry (Hutchinson, 1957). The topographic, geologic, biologic, and cultural characteristics that are significant are partially known from watershed studies in the United States (Norton, 1982; Loucks and Odum, 1978), Canada (Harvey *et al.*, 1981) and Europe (Drablos and Tollan, 1980). Accordingly, a series of quantifiable measures for the 267 watersheds in northeastern Minnesota were defined and evaluated through a combination of field, cartographic, and laboratory methods.

The measurement procedures for a number of key variables are briefly summarized in the following two sections; other procedures and more detailed methodology and quality assurance reports are available from the authors (Liukkonen *et al.*, 1985; Glass *et al.*, 1983). In general, measurements were replicated by systematic and random sampling and usually agreed within 5%–10% of initial values.

Watershed Parameters

Atmospheric inputs are represented by precipitation volume and chemical composition. Annual precipitation, evapotranspiration, and runoff were determined for each watershed from water atlases (Geraghty *et al.*, 1973; Lindholm *et al.*, 1979; Ericson *et al.*, 1979). Total wet sulfate deposition was calculated by linear interpolation between deposition fields given in Chan *et al.* (1983).

Area, topographic, and hydrologic parameters, such as number of inlets and outlets, bathymetry, and streamflow magnitude were measured from the most current 1:24000 scale USGS topographic maps available. Hydrologic type is adapted from the classificaton used by Eilers *et al.* (1983), Black *et al.* (1963), and Andrews and Threinen (1966) and is determined by the presence or absence of channelized surficial inlets and outlets. Lakes with no surface inlets or outlets are defined as "seepage"; lakes with no inlets and a permanent outlet are defined as "headwater" (equivalent to "spring" in Eilers' classification); lakes with both inlet(s) and outlet(s) are defined as "drainage"; and lakes with inlet(s) but no outlet(s) are defined as "inflow." Field checks were performed on 12 lakes and cartographic representations were generally found to be correct, but small intermittent streams were occasionally not marked on the maps and recent work by beavers had altered drainage patterns somewhat at 2 of the smaller lakes.

Total streamflow magnitude, adapted from Winter's (1977) streamflow magnitude, combines the number of streams and cartographic size representation as a surrogate for flow measurements. Each stream inlet and outlet was multiplied by a constant determined by the manner in which the stream was depicted on the map: a double line implied a large-volume stream and was

assigned a 4, and a single line stream and intermittent stream were assigned a 3 and 2, respectively. The sum of all inlets or all outlets, multiplied by the appropriate constant, is equal to total streamflow magnitude. The absence of streams is indicated by a streamflow magnitude of 1.

Hydrologic inputs were calculated based on average annual precipitation multiplied by watershed area and are used to estimate lake water renewal time. For these calculations, all precipitation that falls on the watershed (less evapotranspiration) was assumed to reach the lake, either through overland runoff or channelized flow. Given the geomorphology of the region, with shallow glacial deposits overlying impermeable bedrock, the volume of groundwater losses or inputs compared with surface inputs was assumed to be small and was excluded from the renewal time estimations. Renewal time was calculated as the volume of the lake divided by the watershed inputs and is reported in years. To assess the dependability of these data, the method was applied to lakes in the Experimental Lakes Areas (ELA), Ontario, for which renewal times had been determined using guaged flow measurements. The mean difference between the calculated values and those based on actual measured flow data was 0.7 yr for lakes with renewal times from 1 to 7 yr (standard deviation = 0.874 yr).

When lake bathymetry maps were available, mean depth was determined using a modified Omernick method (Omernick and Kinney, 1982). When bathymetry was unavailable, mean depth values were compiled from the Minnesota Department of Natural Resources (MDNR) or the Minnesota Land Management Information System (MLMIS) or were calculated from their maximum depths using regression equations based on surface area and maximum depth for lakes of known mean depths. Lake volume was calculated as mean depth multiplied by lake surface area.

In some regions the surface deposits and bedrock are of primary importance in determining lakewater chemistry (Zimmerman, 1982). The rock-weathering literature (e.g., Keller, 1957; Correns, 1963; Nesbitt and Bricker, 1978; Johnson, 1984) can be relied on for a first approximation of rock/acid interactions. However, it is essential that rock/acid interactions be scaled to allow use in statistical studies. For example, the comparison of alkalinity values in a "granitic terrain" with alkalinity values in a "limestone terrain" is awkward without some measure of the relative difference in neutralizing capacity of these bedrock types. In addition, most watersheds have more than one rock type present. In order to improve this comparison, an ordinal scale of acid neutralizing capacity based on rock weathering was created (Table 2) prior to examining the data on lake chemistry and watershed geology. This scale represents a quantification of the relative neutralization capacities and weathering rates of various types of bedrock and regolith. Rock/

Table 2. Rock Neutralization Capacity Scale.

Scale	Igneous Rocks	Metamorphic Rocks	Sedimentary Rocks	Surficial Deposits	
1		Marble	Limestone Dolomite Marl	Calcareous Till Calcareous Alluvium Calcareous Outwash	(more than 10% Carbonate)
2			Dolomite Marl	Calcareous Till Calcareous Alluvium Calcareous Outwash Calcareous Loess	(3–10% Carbonate)
3			Calcareous Shale (1–3% Carbonate)	Till Alluvium Outwash	(1–3% Carbonate)
4		Calcareous Slate (1–3% Carbonate	Shale	Clayey Till Clayey Alluvium Lacustrine Clays	(more than 25% clay)
5	Ultramafics (Dunite, Peridotite)		Calcareous Graywacke Calcareous Arkose Calcareous Quartz Sandstone	Till Alluvium	(10–25% clay)
6	Basalt, Anorthosite, Greenstone, Gabbro, Diabase	Schist		"Mafic" Alluvium "Mafic" Outwash	
7	Grandoiorite, Dacite, Monzonite	Granite Gneiss	Quartz Siltstone	Loess	
8	Syenite, Trachyte, Granite	Slate	Arkose	"Felsic" Alluvium "Felsic" Outwash	
9	Felsite, Rhyolite	Siliceous Slate Cherty Iron Formation	Graywacke		
10		Quartzite	Quartz Sandstone	(Peat)	

acid neutralizing reactions represented in this scaling involve (1) the dissolution of carbonate minerals, (2) the dissolution of Fe, Mn, and Al oxides, (3) the dissolution of alumino-silicate minerals, (4) available bicarbonate, and (5) adsorption on oxides and silicates (Kramer, 1978). The ordinal relationships in Table 2 are based on generally accepted relationships in rock weathering, the special significance of carbonates and clays, and the relative availability of Ca and Mg. Bedrock units in northeastern Minnesota range from 5 to 10 on the scale, with most between 6 and 8, because only igneous and metamorphic rocks with low neutralizing capacity occur in the study area.

Surficial deposits, forest cover, and land-use data covering the state of Minnesota had been previously compiled from various sources and synthesized into a comprehensive computerized database on MLMIS. Watershed boundaries for the Minnesota study lakes were digitized into the MLMIS computer system enabling the retrieval of soils, vegetation, and land-use data (as percentages). MLMIS-derived data were available for all but 19 border watersheds (where data for the Canadian portions were not available). A detailed account of MLMIS data categories and ranges may be obtained from the MLMIS Manual 40 (MLMIS, 1980). Road data and dwelling counts were measured from the most current USGS 1:24000 topographic maps available. Dwelling ratio is calculated as the number of dwellings within 305 m of the lakeshore per hectare of lake surface area.

Water Quality Parameters

Sampling of the study lakes began in the fall of 1978 and continued until the summer of 1983. *In-situ* measurements and 4-L water samples were collected at mid-lake at a depth of 1 m during spring and fall turnovers when the lake was well mixed. Temperature and conductivity profiles were measured; when gradients were detected, additional samples were taken at mid-depth and 1 m above the bottom. Replicate samples were taken at every tenth site. At the end of each day field lab measurements of pH, redox, and conductivity were made, unfiltered aliquots for metal analyses were acidified to 0.2% with concentrated HNO_3 (regarded as total acid exchangeable), and subsamples were filtered for chlorophyll-*a* analysis. The remaining water was kept cold and dark and transported daily to ERL-D for detailed lab analysis. Upon arrival at ERL-D, samples were usually analyzed within 24 h for alkalinity, pH, conductivity, color, and turbidity.

All samples were analyzed in accordance with U.S. EPA Methods for Chemical Analyses of Water and Waste (U.S. EPA, 1979). Ions were measured at ERL-D by a Dionex Model 12 ion chromatograph, conductivity bridge (model CDM 83), Radiometer pH meter and glass electrode (model M64), and autoburette (model ABU 80); acid neutralization capacity was determined by titration and Gran endpoint detection (Stumm and Morgan, 1981); metals were analyzed at the Environmental Research Laboratory–Corvallis (CERL) by inductively coupled plasma emission (Bausch and Lomb Model QA-137) and at ERL-D and CERL by atomic absorption spectrometry (Perkin Elmer Models 403 and 5000); nutrients and chlorophyll-*a* were measured using Standard Methods (APHA, 1980) at the USFS laboratory, Winton, MN; and total organic carbon was determined using an Ionics Model 1258 carbon analyzer at the Department of Chemistry, University of Minnesota–Duluth.

The water quality data have been subjected to quality assurance procedures for single parameter measurements and interrelationships to determined outliers and systematic errors in measurement or manipulation using charge balance (APHA, 1980), calculated pH-alkalinity (Stumm and Morgan, 198!), and comparing measured versus calculated conductivity (Quint and Viallard, 1978). The precision and accuracy (based on standard additions and U.S. EPA and NBS standard samples) of these measurements are, on average, within 5% of expected values. The water chemical data are given as mean values averaged from all samples taken over the 5-year period of study (Glass *et al.*, 1983). The mean for pH values was determined by averaging hydrogen ion concentrations.

Data Analysis Methods and Hypotheses Testing

Given the broad range of watershed data, the steps used in examining the effects of atmospheric inputs and watershed properties on lake chemistry should be considered systematically. To enhance the potential for explanation of the observed responses, credible causal mechanisms must be identified. Each mechanism should be associated with a physical, chemical, or biological linkage by which the influence of the watershed factor will be expressed in lake chemical characteristics. A large number of watershed properties can be considered in an unstructured multiple regression analysis to test how well they account for variation in observed responses. However, this approach leaves the possibility that no physical reason may be evident to explain why certain variables control the response. Indeed, with so many variables, the likelihood is high that some of the strong relationships would be the result of accidental colinearity among variables in the database.

Although color, sulfate, and alkalinity have potential interrelationships, each is also likely to be influenced independently by the various inputs and watershed processes that can influence concentrations in the lake. Thus, a goal of data analysis is to consider as many measurable inputs or watershed factors as possible for which there is evidence to suggest that physical, chemical, or biological processes might exert significant con-

trol over lake water concentrations. To account for the observed lake water chemistry we considered the total atmospheric input and the potential for dilution and concentration through runoff, recharge, weathering, adsorption on land cover, and land use (Table 1).

A variety of statistical procedures are relevant to the simultaneous testing of hypotheses. Eilers *et al.* (1983) used discriminant analysis methods, Haines and Akielaszek (1983) used principal components and canonical analysis, and Thornton *et al.* (1982) used largely single-factor correlations. All these approaches were considered for the Minnesota analysis but were rejected after trial testing because multiple causal mechanisms are not examined as explicitly as in the multiple-regression approach adopted here.

The statistical evaluations were carried out in four stages: The first involved examination of variable distributions. The second was development of a correlation matrix to identify the strength of relationships between variables. This identification led to the third step, which was the selection of a smaller number of variables for more intensive analysis, evaluation of outliers, and data transformations. Log transformations were performed on data, where appropriate, to increase the normality of the distribution. The fourth step was the linear multiple-regression analysis.

Results

Data Distribution

Table 3 summarizes the measured characteristics for 267 watersheds in the study area. Individual watershed characteristics are listed under the nine major classes set forth in the conceptual model (Table 1) preceded by the lake water chemistry parameters. All individual, site-

Table 3. Summary of watershed characteristics for 267 lakes in northeastern Minnesota.

Factor Group and Variable	N	Median	Mean	Minimum	Maximum	Standard Deviation
Lake Water Chemistry						
Alkalinity, mean for the site – μeq/L	267	192.5	259.5	47.33	1,297	209.6
pH – averaged value – pH units	267	7.0	7.1	6.0	8.2	0.425
Conductivity, 25°C corrected – μS/cm	267	34.20	40.67	15.00	128.4	19.77
Color, unfiltered – Pt-Co units	263	27.00	38.08	0.0	195.0	32.96
Sulfate – mg/L	244	3.97	4.14	1.17	10.29	1.271
Chlorophyll-*a*, acid corrected – μg/L	256	4.18	5.13	0.60	38.50	4.044
Organic carbon, total – mg/L	243	7.8	8.3	2.1	30.3	3.95
Iron, total acid exchangeable – mg/L	261	0.15	0.19	0.005	1.13	0.18
Aluminum, tot. acid exchange. – mg/L	261	0.06	0.08	0.005	0.83	0.08
Atmospheric Inputs						
Evaporative concentration ratio	267	2.43	2.60	1.76	3.71	0.54
Annual precipitation – m/yr	267	0.72	0.72	0.69	0.76	0.01
Annual evaporation – m/yr	267	0.4	0.4	0.3	0.5	0.1
Wet-deposition sulfate – g/m^2.yr	267	1.2	1.8	0.9	1.4	0.1
Area						
Lake surface area – ha	267	112.5	834.8	1.2	89.4×10^3	5.7×10^3
Immediate watershed area – ha	267	306.6	16.8×10^2	1.2	16.8×10^4	10.7×10^3
Total watershed area – ha	267	941.9	61.3×10^2	8.8	38.6×10^3	32.3×10^4
Total/surface area ratio	267	8.6	70.1	2.3	3,199.0	275.3
Immediate/surface area ratio	267	2.5	2.8	1.0	8.6	1.2
Relief						
Site elevation – m	267	441.9	446.6	337.7	591.6	61.0
Immediate watershed relief – m	267	46.5	50.0	0.0	155.1	27.4
Total watershed relief – m	267	66.1	86.8	7.6	332.8	64.1
Hydrology						
Site order	267	2.1	4.8	1.0	35.0	6.8
Number of stream inlets	267	1.4	2.6	0.0	42.0	4.4
Number of bog inlets	267	0.5	0.9	0.0	6.0	1.3
Number of stream outlets	267	0.9	0.9	0.0	2.0	0.4
Number of bog outlets	267	0.1	0.1	0.0	1.0	0.3
Total streamflow magnitude – inlets	267	3.0	8.4	1.0	136.0	14.1
Total streamflow magnitude – outlets	267	3.1	3.0	1.0	8.0	1.1
Annual runoff – m/yr	267	0.3	0.3	0.2	0.4	0.1
Total renewal time – years	267	1.8	3.3	0.01	25.4	4.15
Lake Morphometry						
Maximum depth – m	267	12.0	15.0	1.0	84.0	13.57
Mean depth – m	267	4.6	5.9	0.5	26.3	4.5
Lake volume – m^3	267	50.5×10^5	74.6×10^6	6×10^3	54.7×10^8	39.6×10^7

Table 3. (Continued)

Factor Group and Variable	N	Median	Mean	Minimum	Maximum	Standard Deviation
Bedrock Geology						
% bedrock of scale 5	265	0.0	0.2	0.0	23.8	1.7
% bedrock of scale 6	265	21.0	38.5	0.0	100.0	41.0
% bedrock of scale 7	265	0.0	22.4	0.0	100.0	36.3
% bedrock of scale 8	265	22.2	38.1	0.0	100.0	41.0
% bedrock of scale 9	265	0.0	0.7	0.0	38.0	3.6
Lowest bedrock scale present	265	6.4	6.6	5.0	8.0	0.9
Lowest bedrock scale present and >10%	265	6.4	6.7	5.0	8.0	0.8
Average bedrock scale	265	7.0	7.0	6.0	8.0	0.7
Surficial Deposits						
Lowest soil pH present and >10%	248	5.5	5.5	5.2	5.9	0.1
Lowest soil pH present	248	5.5	5.5	5.0	5.7	0.1
Average soil pH—pH units	248	5.5	5.5	4.9	5.9	0.1
% > 3 meters—depth to bedrock	248	0.0	7.5	0.0	97.9	18.8
% not sand or gravel	248	100.0	95.7	5.0	100.0	14.0
% soils of type SSWL	248	0.0	4.1	0.0	94.9	13.9
% peats	248	0.0	4.4	0.0	50.3	9.1
Land Cover Type						
% pine	248	12.9	22.3	0.0	100.0	25.6
% spruce-fir	248	7.2	17.7	0.0	100.0	24.9
% maple-basswood	248	0.0	0.7	0.0	75.3	5.7
% aspen-birch	248	61.0	56.1	0.0	100.0	30.4
% unproductive forest	248	0.0	0.8	0.0	27.9	2.7
% non-forested	248	0.0	2.3	0.0	25.0	4.1
% upland coniferous	248	34.9	39.9	0.0	100.0	30.1
% upland deciduous	248	62.1	56.7	0.0	100.0	30.2
Land Use						
% forest	248	84.8	83.6	46.2	100.0	11.0
% water	248	14.4	15.6	0.0	49.3	10.8
% marsh	248	0.0	0.5	0.0	23.8	2.2
% cultural development	248	0.0	0.3	0.0	7.1	0.9
Dwelling count	266	0.2	19.5	0.0	1,761.0	118.8
Dwellings/lake surface area ratio	266	0.0	0.02	0.0	0.4	0.05
Total road length*—km	265	0.0	1.5	0.0	85.5	6.84
Minimum road distance*—km	65	0.02	0.06	0.0	1.3	0.17

*Only 65 watersheds included roads

specific watershed, and water quality information is available from the authors.

Within-lake variations of alkalinity, color, and sulfate concentrations were examined for a subset of 24 lakes, sampled an average of 21 times over a 2–5-yr period. The average standard error of the mean of alkalinity, color, and sulfate concentration was 17.9%, 61.3%, and 9.3%, respectively, with the average period sampled equal to 3.4 yr. The high average variability for color is caused by lakes with color values near zero. For 13 lakes with color values greater than 10 Pt-Co, units the average standard error of the mean was 38.3%.

Correlation Matrix

Scatter plots and bivariate correlation coefficients were computed in order to inspect the relationships between the variables. The correlation coefficients, between 63 variables and color, sulfate, and alkalinity, as well as their associated degrees of significance, are shown in Table 4.

Two assumptions are to be kept in mind when interpreting the correlation matrix results: (1) the relationships between the dependent and independent variables were assumed to be essentially linear, and (2) the data were assumed to be approximately normally distributed. These assumptions do not hold in all cases even after appropriate transformation. However, the purpose of the correlation matrix at this stage was not to test the significance of individual relationships as much as to provide validation of the dominant variables identified from the physical and chemical process model discussed above.

Variable Selection

Using both the correlation coefficients for all variables, and the hypotheses regarding watershed control, the next step was to select the independent variables most likely to represent major watershed processes in the statistical examination of variability in lake water chemistry. The selection was guided primarily by the re-

Table 4. The correlation of Minnesota watershed components with lake alkalinity, color, and sulfate.

Indepedent Variables	Dependent Variables		
	Color	Sulfate	Alkalinity
Lake Water Chemistry Factors			
Color	–	−0.28**	−0.30**
Sulfate	−0.28**	–	0.18**
Alkalinity	−0.30**	0.18**	–
Chlorophyll-*a*	0.22**	−0.15**	0.09
pH	−0.52**	0.34**	0.79**
Conductivity	−0.25**	0.30**	0.96**
Organic carbon, total	0.62**	−0.21**	0.05
Iron	0.72**	−0.36**	−0.35**
Aluminum	0.54**	−0.16**	−0.19**
Atmospheric Inputs			
Evaporative concentration	0.19	−0.41**	−0.02
Annual precipitation	−0.11*	0.34**	−0.17**
Annual evaporation	0.17**	−0.39**	−0.01
Wet-deposition sulfate	−0.12*	0.41**	0.02
Area			
Lake surface area	−0.01	0.05	0.04
Immediate watershed area	−0.01	0.06	0.04
Total watershed area	0.06	0.04	0.00
Total/surface area ratio	0.18**	−0.06	−0.03
Immediate/surface area ratio	−0.24**	0.24**	0.10
Relief			
Site elevation	−0.18**	0.36**	−0.10
Immediate watershed relief	−0.33**	0.41**	0.02
Total watershed relief	0.06	0.21**	−0.02
Hydrology			
Site order	0.08	0.06	−0.03
Number of stream inlets	0.04	0.10	0.06
Number of bog inlets	0.22**	0.14**	−0.05
Number of stream outlets	0.07	0.12*	−0.21**
Number of bog outlets	0.06	−0.04	0.07
Total streamflow magnitude – inlets	0.03	0.10	−0.07
Total streamflow magnitude – outlets	0.15**	0.03	−0.18**
Annual runoff	−0.18**	0.42**	−0.02
Total renewal time	−0.47**	0.04	0.08
Lake Morphometry			
Maximum depth	−0.37**	0.26**	0.01
Mean depth	−0.37**	0.27**	0.03
Lake volume	−0.03	0.08	0.05

quirements of the conceptual model, the size and significance of correlation coefficients in the matrix, and the magnitude of intercorrelation within the property classification. The variables meeting these criteria for color, sulfate, and alkalinity, are listed in Table 5.

Data Transformation

The value distributions for each variable were examined for normality before the data were used in regression analysis. Initital examination of SPSS-generated frequency histograms (Nie *et al.*, 1979) revealed that a number of the distributions were highly skewed to the right. Further examination of these distributions using BMDP1R residual plots (Dixon, 1975) was made to identify the variables that were furthest from a state of normality. In these cases it was felt that reducing the range of variation of the distribution by log (base 10) transformation would minimize the effect of extreme outliers in regression analyses. Variables that were log transformed included sulfate, alkalinity, total watershed relief, total streamflow magnitude, total watershed area, maximum depth, renewal time, and chlorophyll-*a*. No outliers were removed from any distribution.

Multiple-Regression Analyses

Evaluations of the degree of association of the selected sets of independent variables with color, sulfate, and alkalinity were conducted in two stages using multiple-regression analysis. The statistical packages used for this phase of the analysis were BMDP9R (all subjects regression) and (BMDP1R) multiple-regression (Dixon, 1979).

The all-subsets regression generated a series of independent variable subsets (sizes ranging from 1 to 10 variables each). A single best subset was selected from this list by choosing the one with the highest adjusted

Table 4. (continued)

Indepedent Variables	Dependent Variables		
	Color	Sulfate	Alkalinity
Geology			
% bedrock of scale 5	−0.09	0.11*	0.19**
% bedrock of scale 6	0.01	0.29**	0.08
% bedrock of scale 7	−0.09	−0.17**	0.21**
% bedrock of scale 8	0.07	−0.14**	−0.27**
% bedrock of scale 9	−0.01	0.06	−0.01
Lowest bedrock scale present	0.08	−0.35**	−0.20**
Lowest scale present and >10%	0.10	−0.36**	−0.18**
Average bedrock scale	0.04	−0.25**	−0.21**
Surficial Deposits			
Lowest soil pH present and > 10%	−0.18**	−0.04	−0.04
Lowest soil pH present	−0.25**	−0.03	−0.06
Average soil pH	0.19**	−0.06	−0.13**
% > 3 meters depth to bedrock	0.22**	−0.08	0.04
% not sand or gravel	−0.14**	0.06	0.02
% soils of type SSWL	0.14**	0.06	−0.04
% peats	0.31**	−0.05	−0.01
Land Cover Type			
% pine	0.02	0.04	−0.03
% spruce-fir	0.05	0.25**	−0.11*
% maple-basswood	−0.04	−0.03	0.05
% aspen-birch	−0.07	−0.22**	0.11*
% unproductive forest	0.28**	−0.19**	−0.09
% non-forested	−0.03	0.01	0.09
% upland coniferous	0.06	0.24**	−0.12*
% upland deciduous	−0.08	−0.22**	0.12*
Land Use			
% forest	0.43**	−0.04	−0.07
% water	−0.48**	0.06	0.07
% marsh	0.19**	−0.09	−0.07
% cultural development	0.05	0.07	0.19**
Dwelling count	0.00	0.04	0.08*
Dwellings/lake surface area ratio	0.07	0.12*	0.13**
Total road length	0.02	0.06	0.11*

*represents significance ≥0.05 and <0.10.
**represents the highest level of significance <0.05.
All other significance values are ≥0.10.

correlation coefficient (adj-r^2) *and* with the absolute values of the *T*-statistic for each variable in the subset being greater than or equal to 2.0 *and* with a Mallow's Cp for that subset approximately equal to the number of independent variables initially introduced in the analysis. It should be noted that there are other methods that might have been used to select a single "best" subset from such a group. One such method (selecting the subset with the highest minimum *T*-statistic with an absolute value ≥2.0) was also evaluated and found to select the same "best" subset as the first method more than 50% of the time. Since a major goal of this study was to account for the maximum amount of variability in the dependent variables, and because the adjusted r^2 of the best subset selected by the second method was never greater than that selected by the first, it was decided that a single "best" subset would be chosen uniformly according to the first method.

The variables found to comprise the best subsets for explaining the variability in color, sulfate, and alkalinity by various hydrologic classes are indicated in Table 6. The lakes were grouped by hydrologic type in order to compare the differences in watershed component effects where hydrologic factors were controlled. Since there were so few lakes in the seepage and inflow classes, they were grouped together for analysis.

Although ten variables were introduced initially in the multiple regression equations for color, three (relief, percent coniferous, and soil-pH) do not occur in the best regression subsets for any hydrologic type grouping. The possibility of co-variation among independent variables may account for their absence. Soil pH, for example, was strongly related to the percentage of peat in a watershed (r = .68) and therefore most likely did not show up as an independent factor in the multiple-regression analysis because it could not account for any

Table 5. Watershed components chosen by property of classification (from Table 1) for use in multiple-regression analyses.

Property Classifications and Independent Variables (Transformations)	Dependent Variables		
	Color (Pt-Co units)	Sulfate ($\log_{10}$ μeq/L)	Alkalinity ($\log_{10}$ μeq/L)
Lake Water Chemistry			
Chlorophyll-*a*			X
Atmospheric Inputs			
Evaporative concentration	X	X	X
Annual precipitation			X
Wet-deposition sulfate		X	X
Area			
Total watershed area ($\log_{10}$ ha)		X	
Relief			
Total watershed relief ($\log_{10}$ m)	X	X	X
Hydrology			
Annual runoff	X		
Total renewal time ($\log_{10}$ yrs)	X	X	X
Lake Morphometry			
Maximum depth ($\log_{10}$ m)	X	X	X
Bedrock Geology			
Percent scale 6 bedrock		X	
Average bedrock scale			X
Surficial Deposits			
Average soil pH	X	X	X
% peat	X	X	X
Land Cover Type			
% coniferous forest	X	X	
% deciduous forest			X
Land Use			
% forest	X		
% marsh	X		X
% cultural development		X	
Total number of independent variables	10	11	12

significant amount of the variability over and above that yielded by its covariate.

Renewal time, annual runoff, and percent forest occurred in three out of the four best subsets for color. The occurrence of percent peat and percent marsh is consistent with the expected importance of incomplete decomposition as a factor influencing color.

Of the eleven independent variables initially introduced into the multiple regression process with sulfate as the dependent variable, only one (soil pH) was excluded from all best subsets. No variable occurred in more than two subsets. Wet deposition of sulfate was commonly among the variables explaining sulfate concentrations in lakes. Evaporative concentration, on the other hand, is inversely related to sulfate concentration in lakes, because evaporation increases to the west across the lake study sites as wet sulfate deposition decreases, accounting for the magnitude of the correlation, −0.95. Bedrock scale 6 (Table 4) is positively correlated with lake sulfate over all watersheds and remains a significant factor in the multiple regression for headwater lakes (Table 6).

Twelve independent variables were used in the best-subset multiple-regression selection process for alkalinity. As with sulfate, no independent variable was found to occur in more than two of the four best subsets. Average bedrock scale is significant when all lakes are considered, but not for any of the smaller groups. On the other hand, wet deposition of sulfate and chlorophyll-*a* (an indicator by biogenic productivity, and over brief periods, of alkalinity) occur in two of the regression models, along with indicators of organic sources of alkalinity, percent peat, and percent marsh.

One reason for focusing on color as one of the three lake water chemistry measures to be evaluated in this study was the potential for organic constituents to contribute to acid buffering capacity and to mediate metal mobilization and potential metal toxicity. Color rather than total organic carbon (TOC) was used in these analyses as a more sensitive measure, but both are strongly correlated. Color, however, is inversely related to alkalinity and more directly related to aluminum and iron than is TOC (Table 4). Within the range of pH at which the bicarbonate alkalinity was measured, there was an indication of buffering provided by the organic compounds contributing color and TOC at the highest

Table 6. Factors identified as belonging to the best subset in multiple regression models for three hydrologic classes of lakes, and all lakes.

	Seepage & Inflow	Drainage	Headwater	All
BEST SUBSETS FOR COLOR				
Evaporative concentration	X	X		X
Annual runoff	X	X	X	
Total renewal time	X		X	X
Maximum lake depth		X		X
% peat		X		X
% forest	X	X		X
% marsh		X		X
Adjusted r^2	0.72	0.62	0.46	0.48
N	39	153	52	244
BEST SUBSETS FOR SULFATE				
Evaporative concentration	X			X
Wet-deposition sulfate		X	X	
Total watershed area		X		
Total watershed relief		X		
Total renewal time			X	
Maximum lake depth		X		X
% scale-6 bedrock			X	
% coniferous forest		X		X
% cultural development		X		X
Adjusted r^2	0.08	0.32	0.44	0.24
N	36	144	46	226
BEST SUBSETS FOR ALKALINITY				
Chlorophyll-*a*	X			X
Evaporative concentration			X	
Annual precipitation		X		
Wet-deposition sulfate	X		X	
Total watershed relief		X		
Total renewal time			X	
Maximum lake depth			X	
Average bedrock scale			X	X
Average soil pH		X		
% peat	X	X		
% marsh		X		X
% deciduous forest			X	X
Adjusted r^2	0.32	0.17	0.38	0.12
N	37	150	51	238

concentrations. The negative relationship between color and alkalinity may be partially causal if one considers the hydrogen ions contributed by incomplete decomposition in the organic soils, and it may be variable due to other factors not contributing strongly to the bicarbonate alkalinity but involving ion exchange reactions of the organic anions in these watersheds.

Across the entire set of study lakes, the multiple-regression model accounts for 48% of the variability in lake color. For headwater lakes 46% of the variability is explained, 62% in drainage lakes, and 72% in seepage and inflow lakes.

For sulfate and alkalinity concentration the variability explained is appreciably higher for the smaller headwater lakes/watershed systems than for the population as a whole. In the headwater systems, 44% of the sulfate variability is explained compared with 24% for all 267 watersheds with bedrock type, renewal time, and sulfate deposition shown to be important correlates. For drainage lakes, 32% of the variability was explained, indicating some loss of correlation as the averaging over larger watersheds increases. The variability in alkalinity explained also is highest (38%) for headwater lakes but only 12% across the entire sample of lakes. Again, the close association of these lakes with bedrock type, deciduous forest, renewl time, lake depth, evaporative concentration, and sulfate deposition seems to account for the higher than average explanation.

The role of lake renewal time as a factor in controlling lake water chemistry was evaluated further by running multiple-regression analysis on three ranges of renewal time for drainage lakes (Table 7). Approximately one-

Table 7. Best subsets and adjusted r^2 for drainage lakes by renewal time.

	Renewal Time Category		
	<8 months	8 months–3 years	≥3 years
BEST SUBSETS FOR COLOR			
Total watershed relief		X	X
Annual runoff	X		
Total renewal time		X	X
Maximum lake depth	X		
Average soil pH		X	
% peat	X		X
% coniferous forest	X		
% marsh	X	X	X
% forest	X	X	X
Adjusted r^2	0.72	0.54	0.58
N	48	56	49
BEST SUBSETS FOR SULFATE			
Evaporative concentration	X	X	X
Total watershed relief	X		
Maximum lake depth			X
% scale-6 bedrock	X		
Average soil pH			X
% coniferous forest			X
% cultural development		X	
Adjusted r^2	0.28	0.20	0.46
N	45	52	47
BEST SUBSETS FOR ALKALINITY			
Chlorophyll-*a*		X	
Evaporative concentration			X
Average soil pH			X
% peat			X
% marsh	X	X	
Adjusted r^2	0.12	0.16	0.34
N	47	54	49

third of the drainage lakes have short renewal times (less than 8 months: mean = 0.13 yr), one-third have medium length renewal times (greater than 8 months and less than 3 yr: mean = 1.3 yr), while the remaining third are characterized by relatively long renewal times (greater than or equal to 3 yr: mean = 5.6 yr) Variation in color was best explained (72%) for drainage lakes with short renewal times, suggesting the possible decomposition of this constituent over the longer renewal times. The variation in both sulfate and alkalinity was best explained (46% and 34%, respectively) in the drainage lakes with long renewal times, apparently reflecting a cumulative or retention component for these two constituents.

Discussion

The goal of this study was to improve understanding of the relationships between measures of lake chemistry and the watershed characteristics potentially associated with them. To this end the means and distributional characteristics of the watershed descriptors were prepared and reviewed for a database on 267 watershed/lake systems. The relationships between the watershed characteristics and the lake response variables were examined using a correlation matrix and multiple-regression analyses. Most of the variation of lake alkalinity and color was accounted for in headwater systems. Atmospheric inputs were significantly related to both lake sulfate and alkalinity concentrations.

Development of the database has identified several important properties of the watershed/lake relationship. The most important concerns the heterogeneity of conditions within a watershed, with extremes tending to balance one another to produce an "average" condition as watershed size increases. The smallest watersheds are most likely to be dominated almost entirely by a single factor such as weathering-resistant bedrock, shallow soil, or coniferous forest. Larger watersheds tend to average several key variables that differ little, or randomly, among watersheds.

Heterogeneity also bears on a second aspect of the data. The MLMIS information was given for many variables as an average for 16.2-ha (40-acre) cells, and for

others, as 259.0-ha (square-mile) cells. These large inventory units produce a composite of conditions in the landscape, with small variation between cells. Because of the averaging of heterogeneous components, use of aggregated data from these relatively large blocks probably does not alter the characterization of watersheds that are several hundred hectares in size or larger. However, these aggregated data reduce the description of small watersheds to the same type of composite as in large watersheds, while the chemistry of the lakes in these small watersheds has the potential to vary more directly in relation to a narrower range of watershed characteristics. As a result, some of the potential signal may be lost for the smallest watersheds.

The relatively modest strength of correlations between lake chemistry and watershed characteristics, as shown in Table 4, is attributable to the large number of variables that influence the biogeochemistry of a watershed and to the composite nature of some of the data used. In spite of these limitations, the correlation values indicate important interrelationships among watershed variables and lake chemistry. Overall, the regressions indicate that, for this Minnesota region, lake sensitivity (as measured by alkalinity) is greatest under high wet-sulfate deposition, low weatherability of bedrock, and a high proportion of peat and marsh in the watershed. Sensitivity is ameliorated by factors related to high levels of chlorophyll-*a*, larger maximum lake depths, long water renewal time, and a high proportion of deciduous forest in the watershed.

The highest correlations between lake sulfate and the watershed components (Table 4) are with atmospheric inputs, relief, and bedrock geology. Nearly all these correlations are at the highest level of statistical confidence. The correlations between wet-sulfate deposition and percent bedrock of scale 6 with lake sulfate are positive 0.41 and 0.29, respectively, and indicates that terrestrial components may be contributing sulfur to the aqueous environment. Gabbroic rocks (scale 6) contain most of the sulfide occurring in northeastern Minnesota and occur on the eastern portion of the study area where atmospheric deposition is highest. The occurrence of bedrock scale 6 is also coincidentally and positively correlated (0.51) with site elevation and (0.33) with percent spruce forest, both of which correlate significantly with lake sulfate and are linked to increased atmospheric inputs.

Dry deposition of sulfate in the region could add 10% to 30% to the wet inputs, increasing in the same west to east vector as the wet inputs (Ragland and Wilkening, 1983). Although this additional source would have to be considered to more completely account for lake sulfate concentration, taking into consideration sulfate retention (Thompson and Hutton, 1985), the similarity in pattern to wet deposition makes substantial improvement in explanation unlikely. Another source of variability in lake water sulfate concentrations may lie in differences in the amount of sulfate reduction to sulfide or elemental sulfur, depending on sediment characteristics or the duration of anoxia in the lake and lake sediments. In-lake processes may contribute part of the variability in sulfate that is not explained by the watershed factors, but, of the three water quality measures, sulfate concentration showed the lowest within-lake variability over time.

The multiple-regression analysis used here provides strong explanation for a lake property such as color that is locally and seasonally generated in the watershed and can decay over time. The explanatory power of the watershed and atmospheric input descriptors is only moderate for sulfate in the lake, however, and is attributable largely to the strong gradient in wet sulfate deposition across the study area and to the lesser influence of bedrock. On the other hand, alkalinity appears to be mostly correlated with relatively local variation in soils and geology, along with the large number of more aggregated variables described here. Explanation of the variability in alkalinity is low using these variables, although for some lake systems, a portion of it is determined by the within-region differences in wet-sulfate deposition. Small and variable volumes of groundwater inputs containing high concentration of alkalinity, not quantatively accounted for in these analyses, undoubtedly play an important role in determining lake chemistry.

The general biogeochemical equation relating atmospheric inputs to watershed processes shows that the resultant water quality of headwater systems is traceable. For large and complex watersheds, we recognize that many of these data are time-series and are dependent upon the watershed history preceding sample collection. Some of the unexplained variability across watersheds may be due to watershed-specific seasonal and long-term processes and to the lack of quantitative data on important variables such as groundwater flow, cation exchange capacity of the soils, and dry deposition.

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References

American Public Health Association/American Water Works Association (1980) *Standard Methods for the Examination of Water and Wastewater*, 15th ed. pp. 30–31. APHA/AWWA, Washington DC.

Andrews, L. M. and Threinen, C. W. (1966) Surface water resources

of Oneida County. Wisconsin Conservation Department, Madison, WI.
Black, J. J., Andrews, L. M. and Threinen, C. W. (1963) Surface water resources of Vilas County. Wisconsin Conservation Department, Madison, WI.
Brosset, C. (1978) Factors influencing pH in lake water, *Water Air Soil Pollut.* **11**, 57–61.
Chan, W. H., Tank, A. J., and Lusis, M. A. (1983) Precipitation concentration and wet deposition fields of pollutants in Ontario, September 1980 to December 1981. ARB-61-83-ARSP, Ontario Ministry of the Environment.
Chen, C. W., Gherini, S. A., Hudson, R. J. M., and Dean J. D. (1983) The integrated lake-watershed acidification study: Model principles and application procedures. EPRI EA-3221, Electric Power Research Institute, Palo Alto, CA.
Correns, C. W. (1963) Experiments on the decomposition of silicates and discussion of chemical weathering. Clays and clay minerals. 10th National Conference on Clays and Clay Minerals, National Academy of Science – National Research Council, Washington, DC.
Dixon, W. J. (1979) BMDP statistical software 1979. University of California Press, Los Angeles, CA.
Drablos, D. and Tollan, A. (1980) Ecological impact of acid precipitation. Proceedings of an International Conference, Sandefjord, Norway, SNSF Project, Oslo, Norway.
Eilers, J. M., Glass, G. E., Webster, K. E. and Rogalla, J. A. (1983) Hydrologic control of lake susceptibility to acidification, *Can J. Fish. Aquatic Sci.* **40**, 1896–1904.
Ericson, D. W., Lindholm, G. F., and Helgesen, J. O. (1979) Water resources of the Rainy Lake watershed, northeastern Minnesota. Atlas HA-556, U.S. Geological Society Hydrologic Investigations, Washington, DC.
Galloway, J. N., and Cowling, E. B. (1978) The effects of precipitation on aquatic and terrestrial ecosystems, *J. Air Pollut. Control Assoc.* **28**, 229–235.
Geraghty, J. J., Miller, D. W., Van Der Luden, F. and Traise, F. L. (1973) *Water Atlas of the United States*. Water Information Center, Inc., New York, NY.
Glass, G. E. (1977) Identification and distribution of inorganic components in water: What to measure? in *Aquatic Pollutants and Biological Effects with Emphasis on Neoplasis*, H. F. Kraybill, ed., *Ann. N.Y. Acad. Sci.* **298**, 31–46.
Glass, G. E. and Brydges, T. (1982) Problem complexity in predicting impacts from altered precipitation chemistry, in *Acid Rain/ Fisheries*, T. A. Haines, and R. E. Johnson, eds., pp. 265–286. American Fisheries Society, Bethesda, Md.
Glass, G. E., Heinis, L., Rogalla, J., Ilse, J., Anderson, L. E., Eilers, J. M., Liukkonen, B., Johnston, P., Sorenson, J., Tongen, S., Gustafson, G., Simmons, F., Loucks, O. and Rapp, G. (1983) Documentation and quality assurance summary for alkalinity, hydrogen ion (pH) and specific conductivity measurements of water quality from selected areas of Minnesota, Wisconsin, Michigan and Ontario. ERL-DUL-523, U.S. Environmental Protection Agency, Environmental Research Laboratory – Duluth, MN.
Glass, G. E. and Loucks, O. L. (1980) Impacts of airborne pollutants on wilderness areas along the Minnesota–Ontario border. EPA-600/3-80-044, U.S. Environmental Protection Agency, Environmental Research Laboratory – Duluth, MN.
Haines, T. A. and Akielaszek, J. (1983) A regional survey of chemistry of headwater streams in New England: Vulnerability to acidification. FWS/OBS-80/40.15, U.S. Fish and Wildlife Service, Eastern Energy and Land Use Team, Washington, DC.
Harvey, H. H., Pierce, R. C., Dillon, P. J., Kramer, T. R. and Whelpdale, D. M. (1981) Acidification in the Canadian aquatic environment. No. 18475, National Research Council Canada, Associate Committee on Scientific Criteria for Environmental Quality, Ottawa.
Hutchinson, G. E. (1957) *A treatise on Limnology*, Vol. 1. John Wiley and Sons, New York, NY.
Johnson, N. M. (1984) Acid rain neutralization by geologic materials, in *Geological Aspects of Acid Deposition*, O. P. Bricker, ed., pp. 37–53. Ann Arbor Science Publications, Inc., Ann Arbor, MI.
Keller, W. D. (1957) The principles of chemical weathering. Lucas Brothers, Columbia, MO.
Kramer, J. R. (1978) Acid precipitation, in *Sulfur in the Environment: Part 1. The Atmospheric Cycle*, J. O. Nriagu, ed., pp. 325–369. John Wiley and Sons, Inc., New York, NY.
Lindholm, G. F., Ericson, D. W., Broussard, W. L. and Holt, M. F. (1979) Water resources of the St. Louis River watershed, northeastern Minnesota. Atlas HA-586, U.S. Geological Survey Hydrologic Investigations, Washington, DC.
Liukkonen, B. W., Ilse, J. A., Webster, K. E. and Glass, G. E. (1985) Documentation of the ERLD-UMD acid rain data bases VIII and IX: Methodology and quality assurance summary for terrigenous and hydrologic watershed variables for the cross-regional data set. EPA-Dul-850A, U.S. Environmental Protection Agency, Environmental Research Laboratory – Duluth, MN.
Loucks, O. L. and Odum, W. E. (1978) Analysis of five North American lake ecosystems: I. A strategy for comparison, *Verh. Int. Verein. Limnol.* **20**, 556–561.
Minnesota Land Management Information System (1980) Manual 40. Land Management Information Center, Minnesota State Planning Agency, St. Paul, MN.
National Research Council (1981) Atmosphere-biosphere interactions: Toward a better understanding of the ecological consequences of fossil fuel combustion. National Academy Press, Washington, DC.
Nesbitt, H. W. and Bricker, O. P. (1978) Low temperature alteration processes affecting ultramafic bodies, *Geochim. Cosmochim. Acta* **42**, 403–409.
Nie, N. H., Hull, C. H., Jenkins, J. G., Steinbrenner, K., and Bent, D. H. (1975) *SPSS: Statistical Package for the Social Sciences*. McGraw-Hill, St. Louis, MO.
Norton, S. A. (1982) Distribution of surface waters sensitive to acidic precipitation: A state level atlas. Department of Geological Sciences, University of Maine, Orono, ME.
Oliver, B. G., Thurman, E. M. and Malcolm, R. L. (1983) The contribution of humic substances to the acidity of colored natural waters, *Geochim. Cosmochim. Acta* **47**, 2031–2035.
Omernick, J. M. and Kinney, A. J. (1982) An improved technique for estimating mean depth of lakes, *Water Res.* **17**, 1603–1607.
Overrein, L. N., Seip, H. M. and Tollan, A. (1980) Acid precipitation-effects on forest and fish. Final report on the SNSF-Project 1972–1980, Oslo, Norway.
Perrin, D. D. and Dempsey, B. (1974) *Buffers for pH and Metal Ion Control*. Wiley, New York, NY.
Quint, J. and Viallard, A. (1978) Electrical conductance of electrolyle mixtures of any type, *J. Solution Chem.* **7**, 533–548.
Ragland, K. W. and Wilkening, K. E. (1983) Intermediate-range grid model for atmospheric sulfur dioxide and sulfate concentrations and depositions, *Atmos. Environ.* **17**, 935–947.
Reuter, J. H. and Perdue, E. M. (1977) Importance of heavy metal-organic matter interactions in natural waters, *Geochim, Cosmochim. Acta* **41**, 325–334.
Schindler, D. W. (1980) Implications of regional-scale lake acidification, in *Atmospheric Sulfur Deposition: Environmental Impact and Health Effects*, D. S. Shriner, et al., eds., pp. 533–538. Ann Arbor Science Publications, Inc., Ann Arbor, MI.
Schnoor, J. L. and Stumm, W. (1985) Acidification of aquatic and terrestrial systems, in *Chemical Processes in Lakes*, W. Stumm, ed. Wiley Interscience, New York, NY, in press.
Schnoor, J. L., Palmer, W. D., Jr. and Glass, G. E. (1984) Modeling impacts of acid precipitation for northeastern Minnesota, *Acid Precipitation Modeling of Total Acid Precipitation Impacts*, J. L. Schnoor, ed., pp. 155–173. Ann Arbor Science Publications, Inc., Ann Arbor, MI.
Shapiro, J. (1966) Yellow organic acids of lake water: Differences in their composition and behaviour. Proc. I.B.P. Symp. Amsterdam, pp. 202–216. U. Minn. Limnological Research Ctr. Series No. 38.
Shilts, W. W. (1981) Sensitivity of bedrock to acid precipitation: Modification by glacial processes. Paper 81–14, Geological Survey of Canada, Ottawa, Canada.
Siegel, D. I. (1981) Effect of snowmelt on the quality of Filson Creek and Omaday Lake, northeastern Minnesota. Water Resources Investigations 81–66, U.S. Geol. Survey, St. Paul, MN.
Sims, P. K. and Morey, G. B. (1972) Geology of Minnesota: A centennial volume. Minnesota Geological Survey, St. Paul MN.
Stumm, W. and Morgan J. J. (1981) *Aquatic Chemistry*, 2nd ed. Wiley Interscience, New York, NY.
Thompson, M. E. and Hutton, M. B. (1985) Sulfate in lakes of eastern Canada: Calculated fields compared with measured wet and dry deposition, *Air Water Soil Pollut.* **24**, 77–83.

Thornton, J. D., Heiskary, S. A., Payer, R. D., and Matta, J. (1982) Acid precipitation in Minnesota. Minnesota Pollution Control Agency (and Minnesota Department of Natural Resources and Minnesota Department of Health), St. Paul, MN.

U.S. Environmental Protection Agency (1979) Methods for chemical analysis of water and wastes. EPA-600/4-79-020, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Office of Research and Development, Cincinnati, OH.

Winter, T. C. (1977) Classification hydrologic settings of lakes in the north central United States, *Water Resources Res.*, **13**, 753–767.

Wright, H. E., Jr. (1972) Physiography of Minnesota, in Geology of Minnesota: A centennial volume, P. K. Sims and G. B. Morey, eds., pp. 561–578. Minnesota Geological Survey, St. Paul, MN.

Zimmerman, A. P. (1982) Final report on sensitivity to acidification of waters of Ontario and neighboring states: II. University of Toronto, Toronto.

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